RI 8823

Bureau of Mines Report of Investigations/1983

Resistance of Selected Refractories to Mineral Waste Melts

By Timothy A. Clancy

UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 8823

Resistance of Selected Refractories to Mineral Waste Melts

By Timothy A. Clancy

UNITED STATES DEPARTMENT OF THE INTERIOR

James G. Watt, Secretary

BUREAU OF MINES

Robert C. Horton, Director

Research at the Tuscaloosa Research Center is carried out under a memorandum of agreement between the Bureau of Mines, U.S. Department of the Interior, and the University of Alabama.

Library of Congress Cataloging in Publication Data:

Clancy, T. A. (Timothy A.)

Resistance of selected refractories to mineral waste melts.

(Report of investigations / United States Department of the Interior, Bureau of Mines ; 8823.

Research performed at Tuscaloosa Research Center.

Bibliography: p. 13.

Supt. of Docs. no.: I 28.27:8823.

1. Refractory materials–Erosion–Testing. 2. Slag. 3. Silicates. I. United States. Bureau of Mines. Tuscaloosa Research Center. II. Title. III. Series: Report of investigations (United States. Bureau of Mines) ; 8823.

TN23.U43 [TA418.26] 622s [666'.72] 83-600263

CONTENTS

ILLUSTRATIONS

TABLES

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	lb/in^2	pound per square inch
g	gram	min	minute
h	hour	µm	micrometer
in	inch	pct	percent
in^2	square inch	rpm	revolution per minute
lb/ft^3	pound per cubic foot	wt pct	weight percent

RESISTANCE OF SELECTED REFRACTORIES TO MINERAL WASTE MELTS

By Timothy A. Clancy[1]

ABSTRACT

In support of research on forming ceramics from mining and processing wastes, the Bureau of Mines tested various commercial refractories to evaluate their resistance to melts of these wastes. Sixteen refractories of various types were exposed in slag erosion tests to two siliceous waste melts with SiO_2/CaO ratios of 4.0 and 2.2. The extent and nature of slag attack were then determined for each refractory. The nature of slag attack was investigated through scanning electron micrographs and microprobe elemental distributions. The refractories that performed best in resisting attack by the melts were high-alumina types, and of the refractories tested, the most resistant was a 90-pct-Al_2O_3, 10-pct-Cr_2O_3 refractory.

[1]Supervisory ceramic engineer, Tuscaloosa Research Center, Bureau of Mines, University, AL.

INTRODUCTION

The Bureau of Mines recently completed a study to determine the feasibility of producing ceramic products using mining and processing wastes found in the United States. Wastes considered as starting materials included slate mining waste, copper mine tailings, and serpentine fines. The results of the study indicated that by making additions to these waste materials and by melting them at temperatures of 1,450° to 1,550° C, both glass and glass-ceramic products could be formed (1).[2]

To support this previous research, evaluation of commercial refractories that could be used for containing the mineral waste melts was needed. The Bureau had earlier evaluated refractories for use with mineral wool melts (2) and coal ash slags (3-4). There have also been many other investigations directed at evaluating refractories in contact with various types of melts or slags. Gilbert (5) determined the slag resistance of refractories to commercial glass and steel slag compositions at 1,540° to 1,700° C and Snajdr (6) and Kennedy (7) evaluated a series of refractories for lining slagging coal gasifiers. Test results obtained in these and similar investigations have generally shown that alumina-containing refractories resist acidic slags best, while magnesia-containing types resist basic slags best. In all cases, refractories with low porosity performed best.

In commercial glass-melting furnaces, which must be built of refractories capable of continuous operation for years, the most widely used refractories are high-alumina types, either sintered or fused; high-chromia types, normally fused; zirconia-containing types, also normally fused; and in some cases, tin oxide-containing varieties.

The purpose of this investigation was to evaluate the relative resistance of a group of selected commercial refractories to highly siliceous melts of mining and processing wastes and to obtain information concerning the mechanism of the slag attack. This report presents the results of the evaluation.

TEST MATERIALS

SLAGS

The wastes used to form molten slags for evaluating the refractories were slate and marble mining waste and copper mine tailings. These materials were modified slightly by the addition of silica, dolomite, or sodium carbonate to produce slag melts with the analyses shown in table 1.

REFRACTORIES

The commercial refractories tested in this investigation can be generally classified in two ways, as sintered or fused-grain rebonded and as high-alumina or basic types. The refractories were selected based on results obtained in earlier Bureau studies (2-4) and outside reports (5-7). The chemical compositions, physical properties, and mineralogies of the 16 refractories evaluated are shown in table 2. The refractories were sintered or rebonded fused-grain products with the exception of refractory A-3, which was a chemically bonded product.

[2]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

TABLE 1. - Partial chemical analyses of waste melts, weight percent

Constituent	SiO_2/CaO ratio of 4.0	SiO_2/CaO ratio of 2.2
SiO_2..........	63.7	48.6
Al_2O_3........	6.7	8.0
CaO..........	15.9	22.0
Na_2O.........	10.4	.7
MgO..........	.3	10.0
Fe_2O_3........	2.9	2.8

TABLE 2. - Refractory properties[1]

Refractory type and sample	Bulk density, lb/ft^3	Apparent porosity, pct	MOR,[2] lb/in^2	Approximate chemical composition, wt pct	Mineralogy
Alumina:					
A-1.....	158.7	13.3	2,300-3,300	58.0 Al_2O_3, 38 SiO_2, 2.4 TiO_2.	Mullite.
A-2.....	170.5	20.6	1,000-1,600	79.0 Al_2O_3, 15.9 SiO_2, 3.0 TiO_2.	Alpha Al_2O_3, mullite.
A-3.....	180.1	17.2	1,800-2,600	82.3 Al_2O_3, 8.3 SiO_2, 5.5 P_2O_5.	Alpha Al_2O_3.
A-4.....	186.2	14.1	3,600	90.0 Al_2O_3, 10.0 SiO_2.	Do.
A-5.....	182.3	19.5	1,000-1,400	88.5 Al_2O_3, 11.0 SiO_2.	Do.
A-6.....	172.5	12.4	3,200-4,200	89.5 Al_2O_3, 9.5 Cr_2O_3.	Do.
A-7.....	195.6	16.4	4,000	99.7 Al_2O_3, 0.1 SiO_2..	Do.
Basic:					
B-1.....	180.4	16.8	2,000-2,700	97.9 MgO, 0.8 SiO_2, 0.6 CaO	Periclase.
B-2.....	184.4	14.2	2,800-3,800	92.6 MgO, 4.4 SiO_2, 1.7 CaO	Do.
B-3.....	187.5	16.5	600- 900	62.0 MgO, 16.0 Cr_2O_3, 12.0 Al_2O_3	Periclase, spinel.
B-4.....	200.0	25.1	900-1,500	39.0 MgO, 25.0 Cr_2O_3, 21.0 Al_2O_3	Do.
Fused:					
F-1.....	183.8	21.3	2,500	92.0 Al_2O_3, 7.0 SiO_2..	Alpha Al_2O_3.
F-2.....	199.3	17.2	4,000	99.6 Al_2O_3, 0.1 SiO_2, 0.1 Fe_2O_3	Do.
F-3.....	211.1	11.4	4,000-5,000	55.0 MgO, 20.0 Cr_2O_3, 11.0 FeO, 8.0 Al_2O_3.	Periclase, spinel.
F-4.....	185.6	19.1	6,800	57.4 Al_2O_3, 28.5 ZrO_2, 12.9 SiO_2.	Alpha Al_2O_3, monoclinic ZrO_2.
F-5.....	188.1	23.9	5,600	48.7 Al_2O_3, 24.3 ZrO_2, 15.0 Cr_2O_3.	Al_2O_3-Cr_2O_3 (solid solution), monoclinic ZrO_2.

[1]Measured by Bureau of Mines except for MOR, which is from supplier data.
[2]Modulus of rupture at room temperature.

The refractories are grouped in table 2 as alumina, basic, and fused types. The alumina types contained from 58.0 to 99.7 wt pct Al_2O_3 and consisted primarily of mullite and/or alpha alumina. The basic bricks contained from 39.0 to 97.9 wt pct MgO and consisted of periclase or periclase with a spinel phase. The fused-grain refractories were two high-alumina bricks (consisting of alpha alumina), a zirconia-alumina-silica brick (consisting of alpha alumina and monoclinic ZrO_2), a zirconia-alumina-chrome brick (consisting of an Al_2O_3-Cr_2O_3 solid solution and monoclinic ZrO_2), and magnesium-chrome brick (consisting of periclase and a spinel phase).

EXPERIMENTAL PROCEDURE

SLAG EROSION TESTS

Rotary slag tests were used to determine the resistance of the refractories to slag erosion. The general procedure for rotary slag testing has been previously described (5, 8) and is schematically illustrated in figure 1. Figure 2 shows the test apparatus used, and figure 3 shows how the samples were arranged for testing. Following assembly of 19 samples in the test drum, the drum was placed onto the drive system and rotated at 6 rpm.

Slag feed was supplied to the rotating drum in the form of extruded pellets that weighed approximately 200 g each. Once the drum had reached the desired test temperature, 400 g of slag feed was introduced at each 10-min interval for the first hour in order to build up a pool of molten slag in the drum. For the rest of each test run, 200 g of slag was fed to the drum at each 10-min interval. The drum was maintained at test temperature by adjusting the flow rates of an oxy-propane burner with an oxygen-to-propane ratio of 2.0. The drum temperature was measured with a radiation pyrometer sighted on the interior refractory face. At the conclusion of each run, the drum was emptied of molten slag and a sample of the quenched slag was obtained for chemical analysis.

Based on preliminary runs, the test conditions were selected. All runs were made at 1,600° C. Test runs 1, 2, 3, and 4 each contained four replicates of four different refractories and three replicates of sample A-4 (table 2), a 90-pct-Al_2O_3 refractory used as a reference standard. These tests were run for 5-h periods using the slag with a SiO_2/CaO ratio of 4.0.

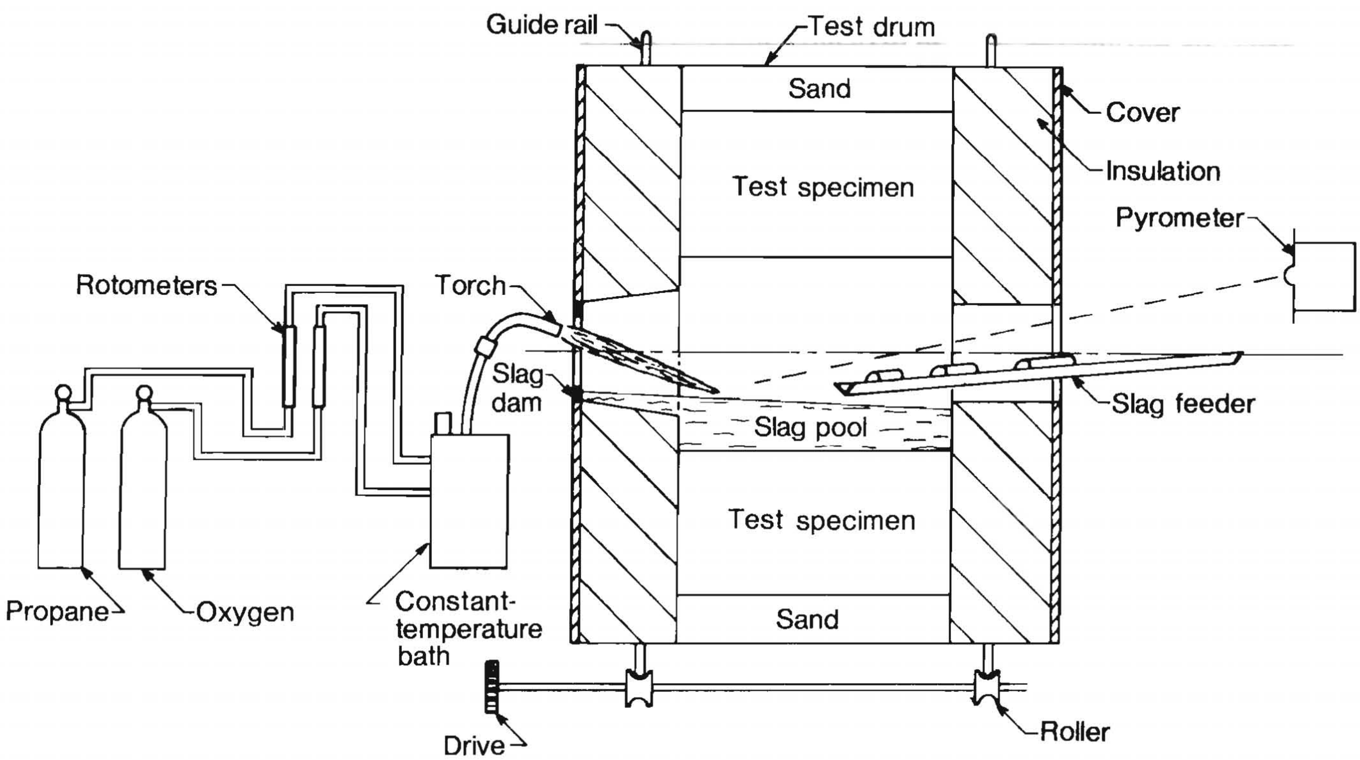

FIGURE 1. - Schematic of rotary slag test apparatus and auxiliary equipment.

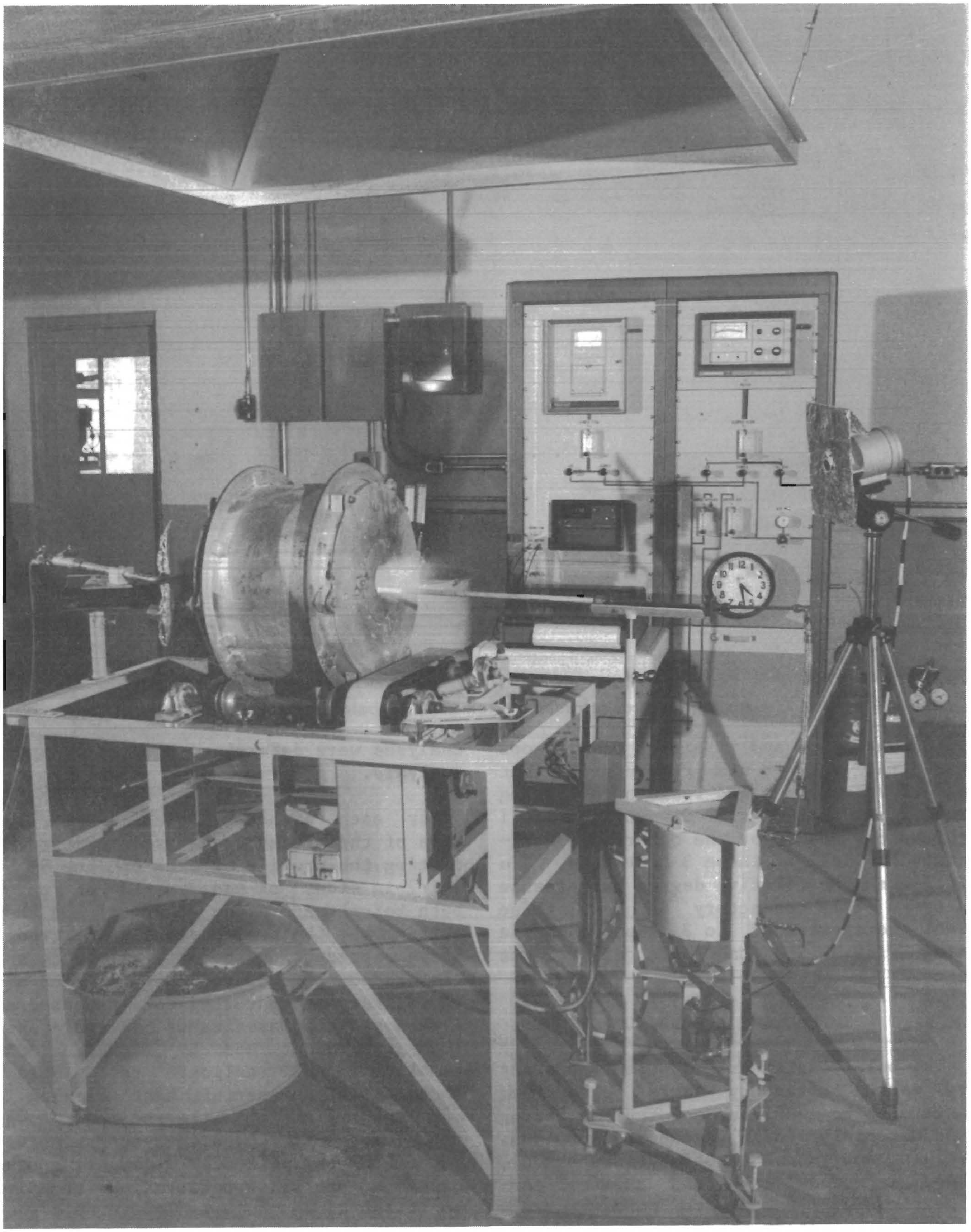

FIGURE 2. - Rotary slag test apparatus.

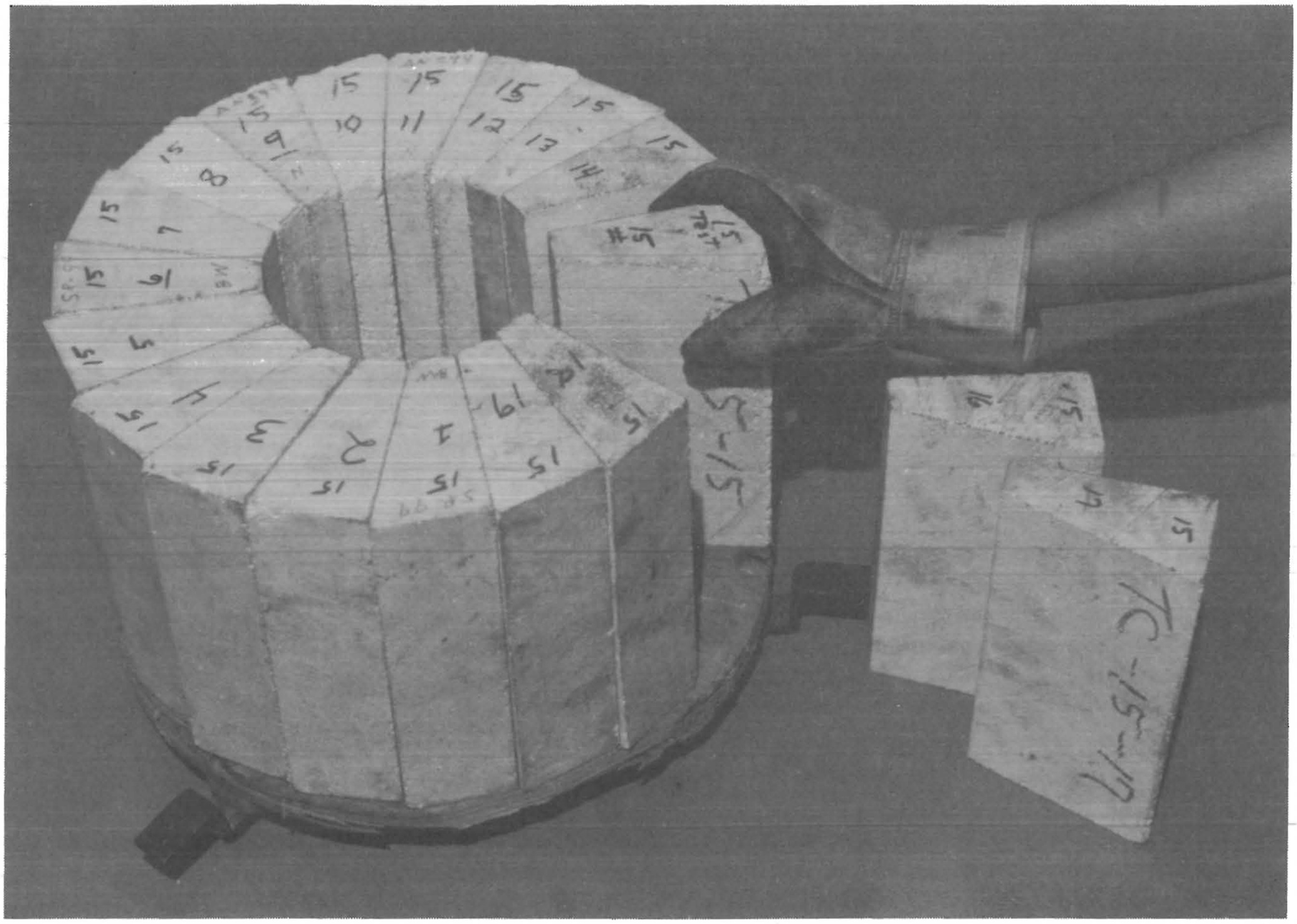

FIGURE 3. - Arrangement of refractory brick samples before placement in test drum.

In runs 5, 6, and 7, direct comparisons were made between six refractories that showed superior slag resistance during the first four runs. Nine bricks of 1 refractory and 10 of the other were evaluated in each of these 3 test runs. To increase the relative degree of erosion between the refractory samples, these runs were extended to 8 h each and the slag with a SiO_2/CaO ratio of 2.2 was used.

REFRACTORY EVALUATION

The bulk density and apparent porosity of each refractory were determined according to American Society for Testing and Materials (ASTM) standard C20-80a. Values for modulus of rupture (MOR), thermal conductivity, and chemical composition were taken from manufacturer's data. Refractory mineralogy was determined by X-ray diffraction, and exit slag analyses were determined by wet chemical analysis.

For each refractory brick sample, the size of the eroded area was determined by tracing the profile of each of the 9- by 4-1/2-in sides of the sample on paper both before and after testing and then cutting out the traced areas. The traced areas representing the original brick and the eroded brick were then weighed and the difference converted and reported as area loss in square inches. Average area loss was determined by averaging the results for all replicate test samples. The smallest number of test samples in any test was three, while the largest was ten. The depth of slag penetration was determined by directly measuring the distance of slag penetration at five locations along the 9-in length of a sample and averaging these values.

RESULTS AND DISCUSSION

SLAG EROSION TESTS

Areas of brick erosion for the alumina refractories evaluated during the first four slag erosion tests are given in figure 4, and results for the basic brick are given in figure 5.

Positive values for brick eroded area (indicating area gain) resulted from the accumulation of a layer of frozen slag on the interior face of the test brick at the end of a test run. After each run, the test chmaber temperature was increased by 100° to 200° C to further fluidize the melt; this helped to ensure clean interior faces after the drum was tilted vertically and emptied. However, retention of a slight accumulation of slag on an interior face could have resulted in a measurement indicating an area gain if very little erosion of the refractory brick had occurred.

All the refractories that demonstrated the best slag erosion resistance consisted primarily of alumina; i.e., 90 pct or greater with the exception of refractory F-5, an Al_2O_3-ZrO_2-Cr_2O_3 fused type. The 90-pct-Al_2O_3, 10-pct-Cr_2O_3 refractory (A-6) had the best slag resistance. These results are consistent with results of previous studies in which alumina refractories showed good slag resistance to highly siliceous, acidic slags. These tests also indicated that sintered refractories with alumina contents of 90 pct or more performed as well as fused refractories of similar chemistry.

The results of the last three runs, which were made to further evaluate refractories that had demonstrated superior erosion resistance in the first test runs, are shown in figure 6. The bricks that eroded least were the Cr_2O_3-containing high-alumina refractories.

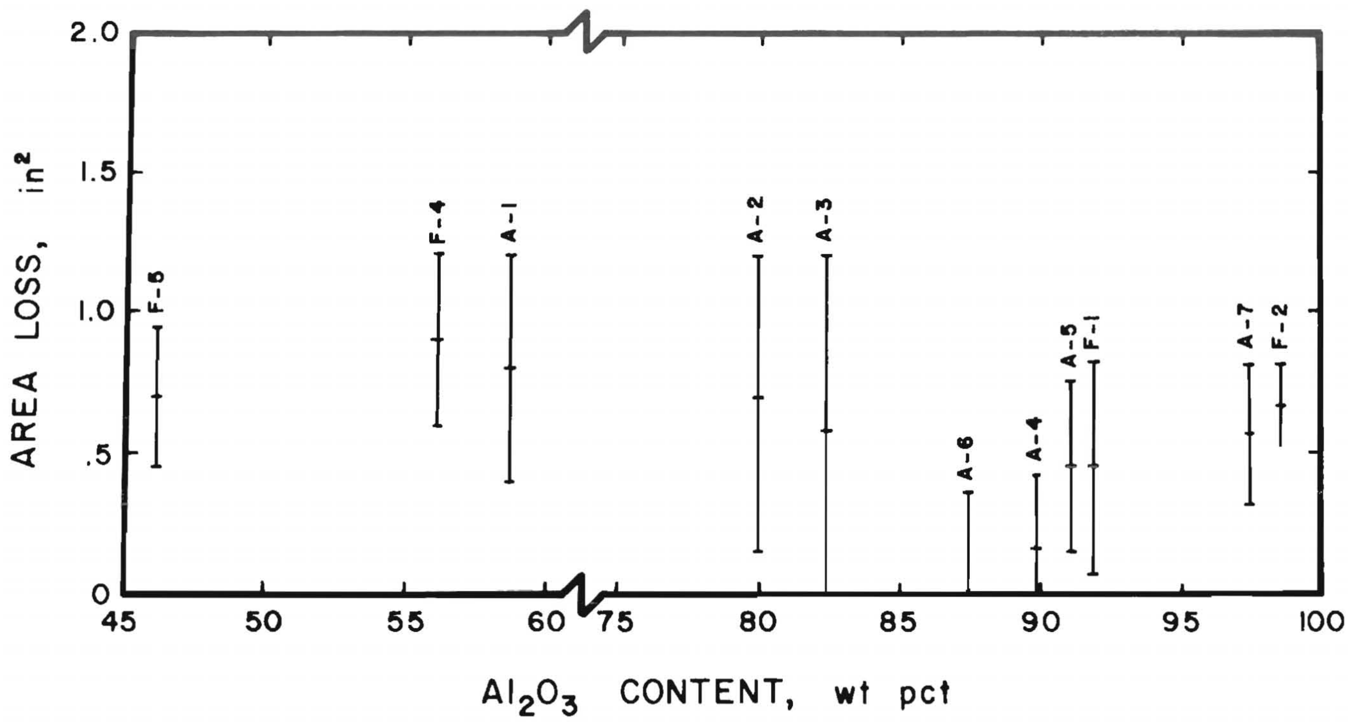

FIGURE 4. - Area losses for alumina refractories. (Data are labeled by sample number.)

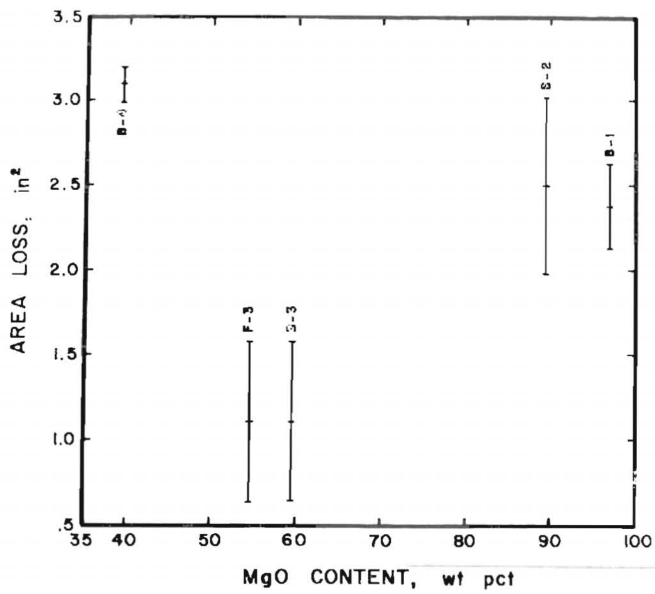

FIGURE 5. - Area losses for basic refractories.

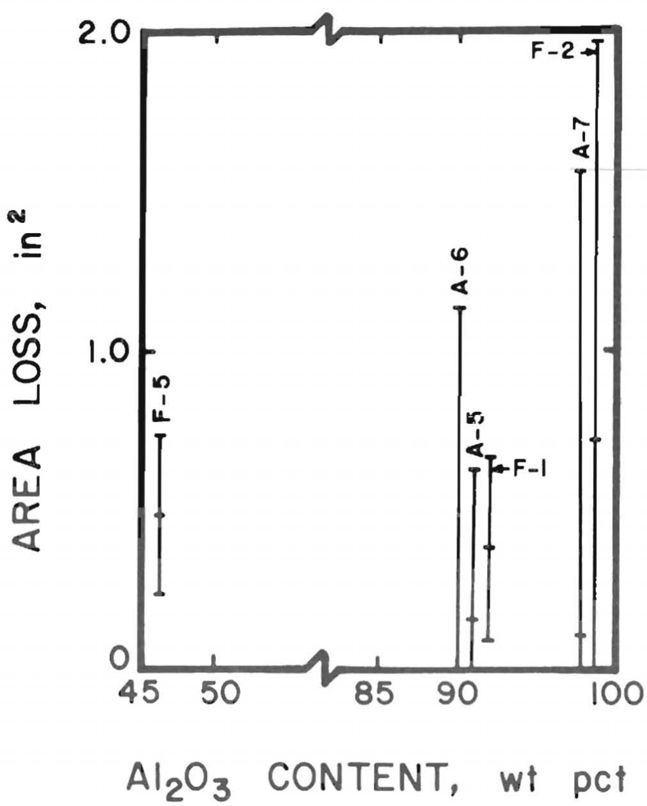

FIGURE 6. - Area losses for refractories which showed superior erosion resistance.

Table 3 shows partial chemical analyses of the slags after the erosion tests. Comparison of the exit slag analyses for runs 1, 2, 3, and 4 to the initial waste melt analyses (table 1) indicates that in three of the runs the major change in melt chemistry was an increase in the Al_2O_3/SiO_2 ratio. In run 3, the major change in melt chemistry was a large increase in MgO content. This change in MgO content supports the high erosion (area) losses recorded for the basic refractories.

TABLE 3. - Partial chemical analyses of slags after erosion tests

Test run[1]	SiO_2	Al_2O_3	CaO	Na_2O	MgO	Fe_2O_3
1.......	57.1	16.0	13.6	6.4	3.6	2.1
2.......	60.4	12.1	14.0	6.7	2.4	3.3
3.......	48.6	10.8	10.5	5.7	17.3	3.7
4.......	55.3	14.0	12.5	7.8	5.0	3.7
5.......	42.9	23.9	11.3	7.3	8.6	4.9
7.......	47.8	17.4	12.1	7.5	8.7	5.6

[1]Slag sample from run 6 was lost.

The appearance of three of the refractories (A-6, F-1, and B-3) after test runs is shown in figure 7. Refractory A-6 shows little slag erosion or penetration was extensive. Refractory B-3 shows poor slag resistance, which is evident from the eroded and rough refractory-slag interface.

Figure 8 presents the depth of slag penetration into various refractories as determined by direct measurement. The sample that exhibited the greatest penetration depth was F-1, a 92-pct-Al_2O_3 fused-grain refractory. While this refractory exhibited one of the lower values for erosion loss, its higher thermal conductivity and porosity (21.3 pct) permitted the slag to penetrate deeper into the brick.

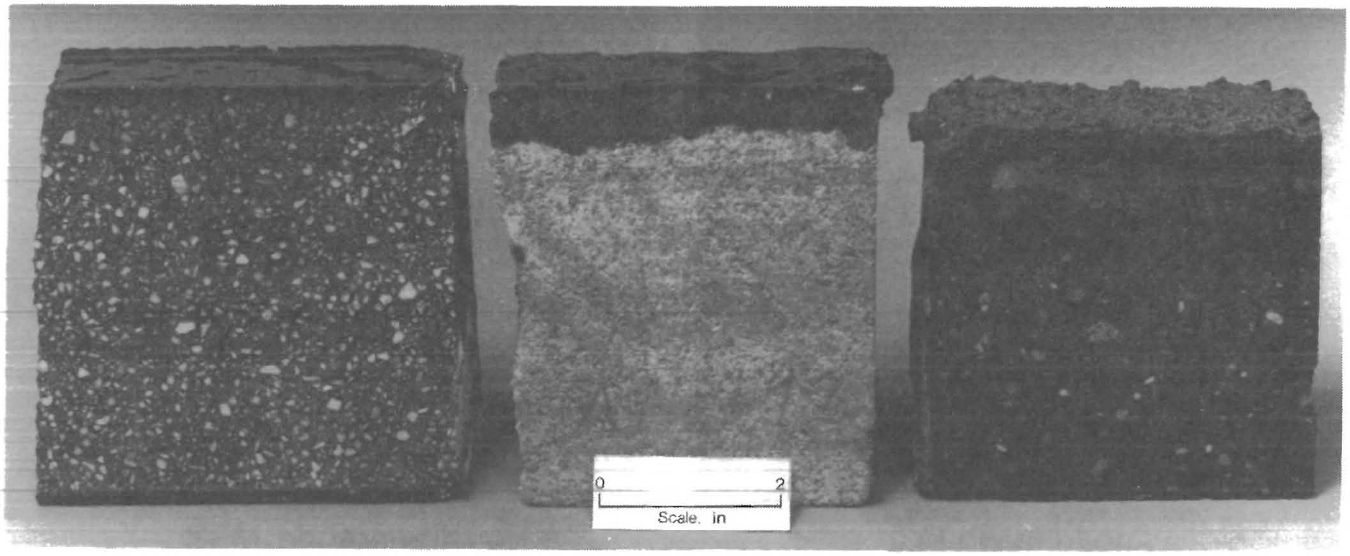

FIGURE 7. - Brick samples showing eroded surfaces. (From left to right, samples A-6, F-1, and B-3.)

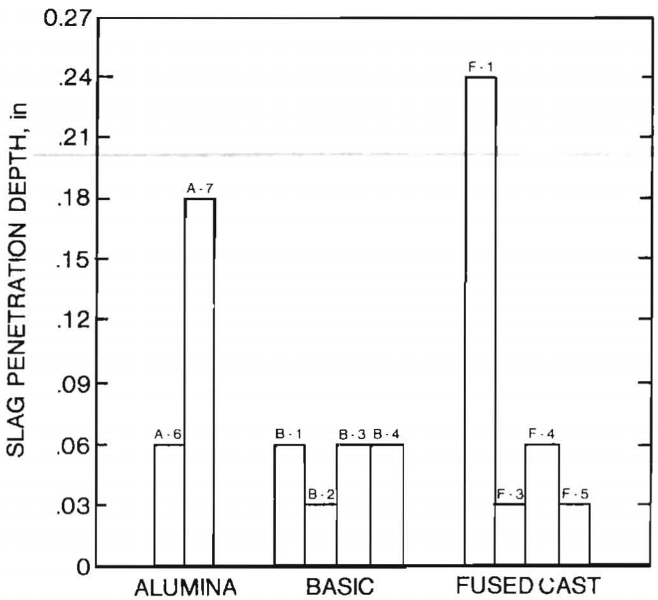

FIGURE 8. - Slag penetration depths for various refractories.

SCANNING ELECTRON MICROGRAPHS

Scanning electron micrographs were taken of three samples of slag-refractory interfaces. The samples selected were A-6 (90 pct Al_2O_3, 10 pct Cr_2O_3), which showed excellent slag resistance; F-1 (90 pct Al_2O_3; fused cast), which showed excellent slag resistance, but also a high degree of slag penetration; and B-3 (60 pct MgO), which showed average slag resistance.

From a comparison of micrographs of samples A-6 (fig. 9) and F-1 (fig. 10), it is clear that slag penetration, as evidenced by Ca diffusion, was less for sample A-6. The Ca distribution for sample A-6 was primarily restricted to a narrow band (about 100 µm) wide) at the slag interface. This observation is consistent with the erosion data, which showed that A-6 had the lowest overall

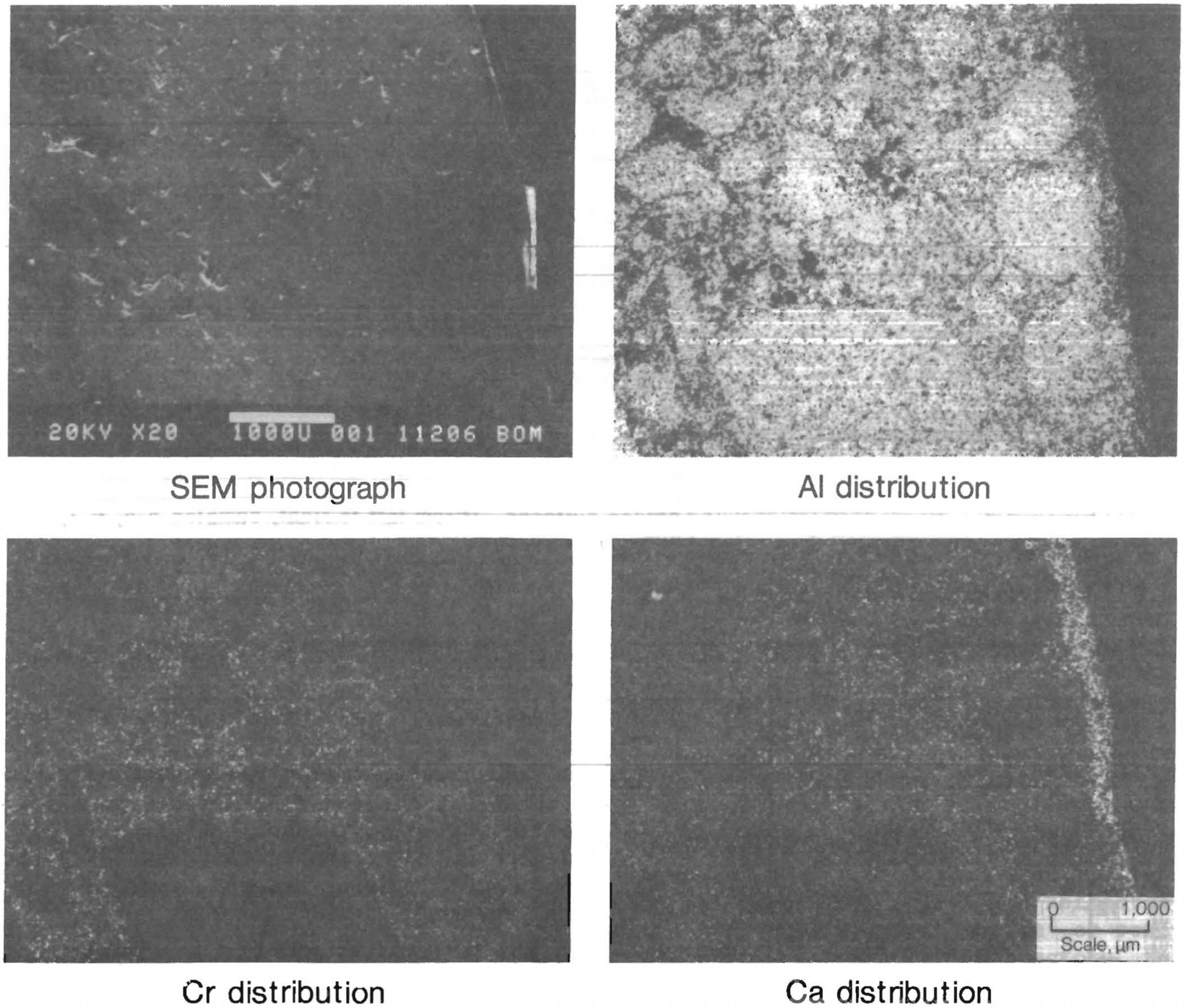

FIGURE 9. - Scanning electron micrographs of elemental distributions at slag-refractory interface, sample A-6.

erosion rate of all the refractories. The limited Ca diffusion and erosion for sample A-6 can probably be attributed to the low porosity of the A-6 brick and the presence of a Cr_2O_3-Al_2O_3 solid-solution bond phase. The micrograph of refractory F-1 indicates extensive Ca and Si diffusion into the sample. However, this refractory had good erosion resistance, as indicated by its average area loss of 0.46 in^2. The deep slag penetration into F-1 was probably a consequence of the relatively high porosity (21.3 pct) and high thermal conductivity of this fused-cast refractory.

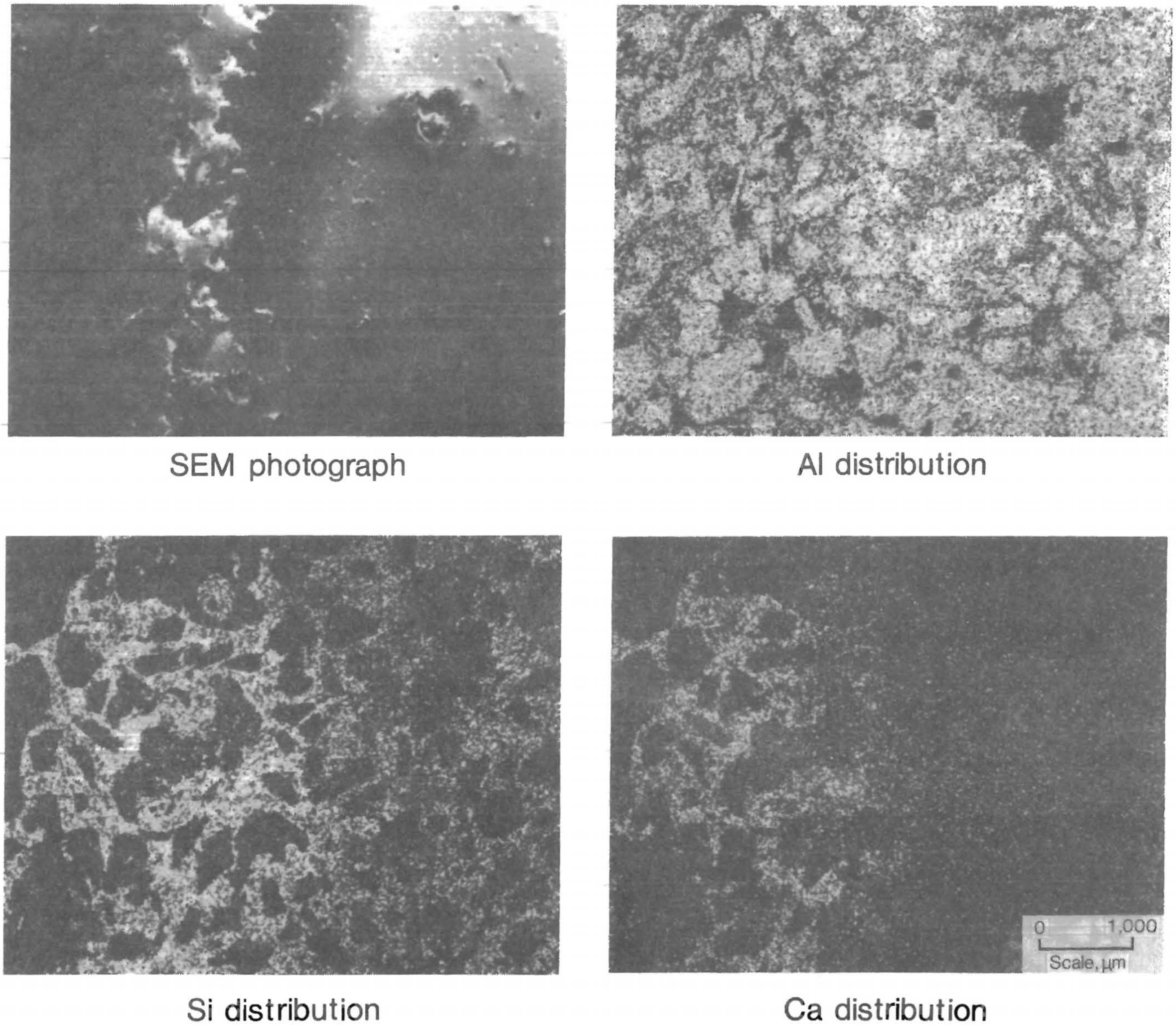

FIGURE 10. - Scanning electron micrographs of elemental distributions at slag-refractory interface, sample F-1.

The micrographs of the basic refractory-slag interface (fig. 11, refractory B-3) clearly show that the extent of Ca diffusion and, thus, slag penetration was slight. The micrographs of this chrome-containing basic refractory indicate that the periclase grains dissolved more readily than the chrome ore grains, which remained as projections at the refractory-slag interface. The micrographs also show the existence of elongated crystals in the frozen slag layer. The elemental distribution scans indicated that these crystals were high in Mg and Ca, and X-ray diffraction indicated the presence of diopside ($CaO \cdot MgO \cdot 2SiO_2$).

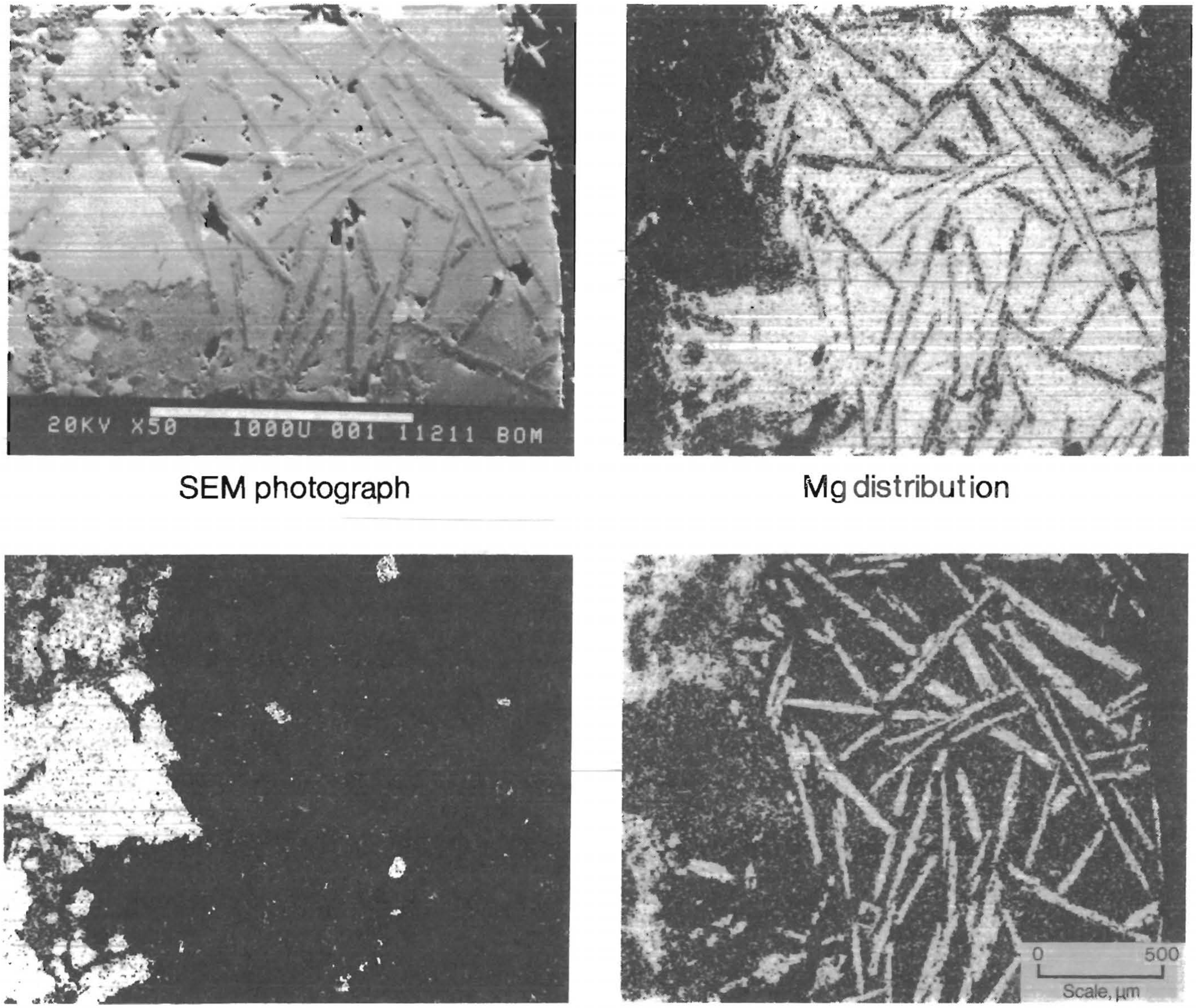

FIGURE 11. - Scanning electron micrographs of elemental distributions at slag-refractory interface, sample B-3.

CONCLUSIONS

Based on the results obtained in tests to determine the slag erosion resistance of 16 different refractories to two highly siliceous melts of mining and process waste materials, the following conclusions can be made:

1. In general, the refractories that performed best in resisting erosive attack by the silicate melts were those with the highest alumina contents (90 to 99 wt pct), including two which also contained Cr_2O_3 additions. A 90-pct-Al_2O_3, 10-pct-Cr_2O_3 refractory had the best slag resistance properties.

2. Slag resistance generally increased as alumina content increased.

3. Fused-grain rebonded refractories were deeply penetrated by slag, yet they had good slag resistance.

4. Basic refractories had the highest rates of slag erosion, but little slag penetration.

REFERENCES

1. Petty, A. V. Producing Centrifugally Cast Glass-Ceramic Pipe From Mining and Processing Wastes. BuMines manuscript in preparation for publication; available for consultation at BuMines, University, AL.

2. Cobble, J. R., and J. P. Hansen. Evaluation of Refractories for Mineral Wool Furnaces. BuMines RI 8090, 1975, 15 pp.

3. Pahlman, J. E., C. F. Anderson, and S. E. Khalafalla. Stability of Alumina-Base Refractories in Western Lignite Ash Slag Environments. BuMines RI 8334, 1979, 16 pp.

4. ______. High-Temperature Corrosion Resistance of Basic Refractories to Coal and Lignite Ash Slags. BuMines RI 8633, 1982, 11 pp.

5. Gilbert, S. V. Rotary Slag Testing of Basic Refractories. Am. Ceram. Soc. Bull., v. 55, No. 7, 1976, pp. 645-648.

6. Snajdr, E. A., B. Klaudinyi, J. A. Middleton, and D. S. Yang. Evaluation of Slag and Refractory Compatibility for Low-Btu Gasification of Coal for Electric Power Generation (U.S. Dep. Energy contract EX-76-C-01-1545 Comb. Eng. Inc.). Dec. 1977, 192 pp.

7. Kennedy, C. R., and R. B. Poeppel. Corrosion Resistance of Refractories Exposed to Molten Acidic Coal-Ash Slags. Interceram., v. 27, No. 3, 1978, pp. 221-226.

8. Cobble, J. R., and L. Y. Sadler, III. A Laboratory Test To Evaluate the Resistance of Refractories to Molten Slags. BuMines RI 8468, 1980, 13 pp.